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ORIGINAL ARTICLE

# Chemoselective one-pot synthesis of 2-phenylamino-5-alkylthio-1,3,4-thiadiazole derivatives from phenylthiosemicarbazide and $CS_2$

**Mohammad Soleiman-Beigi [a,*], Mohammad Alikarami [b], Homa Kohzadi [a]**

[a] *Department of Chemistry, Ilam University, P.O. Box 69315-516, Ilam, Iran*
[b] *Department of Chemistry, Ilam Branch, Islamic Azad University, Ilam, Iran*

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**KEYWORDS**

One-pot;
1,3,4-thiadiazole;
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**Abstract** A novel and fairly efficient chemoselective one-pot method has been developed for the synthesis of both 2-phenylamino-5-alkylthio-1,3,4-thiadiazole and bis-(2-phenylamino-5-alkylthio-) 1,3,4-thiadiazole derivatives from phenylthiosemicarbazide and $CS_2$.


## 1. Introduction

Nitrogen heterocycles are of special interest because they constitute an important class of natural and nonnatural products, many of which exhibit useful biological activities. Among these nitrogen heterocycles are 1,3,4-thiadiazole-containing compounds (Ameen and Qasir, 2012). 1,3,4-Thiadiazole is a kind of five-membered heterocyclic compound containing one sulfur and two nitrogen heteroatoms. The 2,5 positions on 1,3,4-thiadiazole and its derivatives can participate in many chemical reactions (Yuting et al., 2011). The methods of synthesizing substituted thiadiazolines have attracted considerable attention in recent decades. These compounds have gained prominence by exhibiting a wide variety of biological activities as well as producing useful intermediates in several organic preparations (Kumar et al., 2011; Aly and Elsayed, 2006; Abdel-Hamid et al., 2007; Almajan et al., 2005). A large number of uses of 1,3,4-thiadiazoles have become apparent in diverse areas, including the dyestuffs industry (Maradiya, 2002), agriculture (Hatzios et al., 1980) and a variety of other industries as corrosion inhibitors (Chen et al., 2012). Numerous 1,3,4-thiadizoles have been synthesized and reported for various medical uses, such as antitumor (Zhao et al., 2012), antimicrobial (Kharb et al., 2011), antituberculosis (Foroumadi et al., 2006), antidepressant (Yosuf et al., 2008), and anti helicobacter pylori (Foroumadi et al., 2008).

In recent years, attention has been increasingly paid to the synthesis of bis-heterocyclic compounds, which exhibit various biological activities (Dabholkar and Ansari, 2008).

A variety of synthetic methods for the preparation of 1,3,4-thiadiazoles have been reported. One of the most common procedures involves the cyclization of 1,2-diacylhydrazine or its thia-analog in the presence of a coupling agent, such as $SOCl_2$ or $POCl_3$, and a mineral acid (Al-Omar et al., 2004; Serban et al., 2011). Symmetrical 2,5-disubstituted-1,3,4-thiadiazoles were prepared by the condensation reaction of aryl

* Corresponding author.
E-mail address: soleimanbeigi@gmail.com (M. Soleiman-Beigi).
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aldehydes, hydrazine hydrate, and sulfur in ethanol under microwave irradiation (Lebrini et al., 2005).

Oruc et al. (2004) prepared 1,3,4-thiadiazoles in four steps utilizing acyl halides and aryl isothiocyanates. Synthesis of these compounds was also achieved using the reaction of 1,3,4-oxadiazoles with thiourea (Padmavathi et al., 2009).

There are many reports on the synthesis of 1,3,4-thiadiazoles, but few methods for the synthesis of 2-aryl(alkyl)amino-5-alkylthio-1,3,4-thiadiazoles and bis-2-amino-1,3,4-thiadiazoles are reported.

Indukumari et al. (1981) have synthesized 5-alkylmercapto-2-amino-substituted-1,3,4-thiadiazol under acidic conditions by the elimination of ammonia. A robust protocol for the solid phase synthesis of 5-alkyl/aryl-2-alkylamino-1,3,4-thiadiazoles from resin-bound thiosemicarbazides was described (Severinsen et al., 2005).

Kilburn et al. (2003) reported the synthesis of 2-aryl(alkyl)amino-5-alkylthio-1,3,4-thiadiazole derivatives through a reaction of an aldehyde with a thiosemicarbazide bound to a resin, followed by cyclization of the resulting thiosemicarbazone with a solution of iron(III) chloride in dichloromethane/methanol. Er et al. (2009) reported that when trans-1,4-dichloro-2-butane is treated with KSCN, trans-1,4-dithiocyanato-2-butane is formed. Subsequently bis-2-amino-1,3,4-thaidiazole is obtained from the reaction of trans-1,4-dithiocyanato-2-butane with thiosemicarbazide. In general, most of the reported protocols are time-consuming, laborious, and consist of multiple synthetic steps.

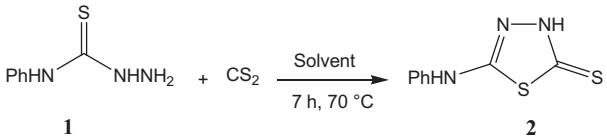
## 2. Results and discussion

Herein, we explore a one-pot method for the chemoselective synthesis of new 2-phenylamino-5-alkylthio-1,3,4-thiadiazole **4** and bis-1,3,4-thiadiazole **6** derivatives from phenylthiosemicarbazide **1** and carbon disulfide under mild reaction conditions.

To optimize reaction conditions in order to determine the effective solvent, time, and temperature in the first step of the procedure (1,3,4-thiadiazole ring closure), the reaction of phenylthiosemicarbazide **1** and $CS_2$ under catalyst free conditions was studied as model reaction (Scheme1).

As shown in Table 1, the optimal result was obtained in DMF at 70 °C. After the ring closure was completed (7 h), alkyl halides **3(a–g)** and $Et_3N$ were added to the reaction mixture and it was monitored using TLC until the second reaction of the procedure was completed (Scheme 2, Table 2).

To test the generality of this procedure under optimal one-pot conditions, we have examined the reaction of phenylsemicarbazide with $CS_2$ and varieties of alkyl halides, such as α-halo acid and ester, alkyl, benzyl, and allyl halides (Table 2). The thiol (thione) functional group was alkylated chemoselectively via the reported one-pot protocol with good to high yields (70–85%), while the *N*-alkylated side products were not observed.




1 2

**Scheme 1** Optimization the reaction conditions.

**Table 1** Seeking the suitable solvent for the one-pot synthesis of 5-phenylamino-1,3,4-thiadiazole-2-thione **2** from phenylthiosemicarbazide at 70 °C in 7 h.

| Entry | Solvent | Yield (%)[a] |
|---|---|---|
| 1 | $CH_3CN$ | 23 |
| 2 | $PhCH_3$ | N.R |
| 3 | $H_2O$ | Trace |
| 4 | $CH_2Cl_2$ | N.R[b] |
| 5 | MeOH | 15 |
| 6 | EtOH | 10 |
| 7 | DMF | 93 |
| 8 | DMSO | 39 |

[a] Isolated yield.
[b] No reaction.

Bis-heterocyclic compounds have been recently noted due to their potential biological and pharmaceutical activities (Palekar et al., 2009). Herein, the proposed procedure was employed successfully for the chemoselective one-pot synthesis of new bis-(2-phenylamino-5-alkylthio)-1,3,4-thiadiazole **6(a–d)** derivatives from the reaction of phenylthiosemicarbazide **1** with carbon disulfide and alkyl dihalides **5(a–d)** in optimized reaction conditions (Scheme 3, Table 3).

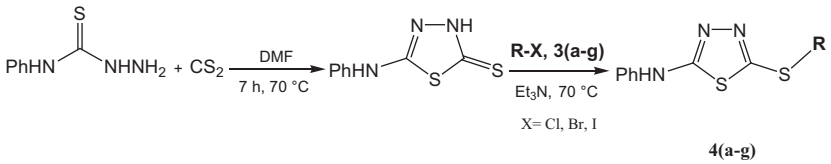
## 3. Experimental

### 3.1. General

All chemicals were purchased from Merck, Fluka, and Aldrich chemical companies. Yields refer to isolated products. Melting points were determined by an Electrothermal 9100 apparatus and are reported uncorrected. The IR spectra were obtained using a FT-IR Hartman-Bomen spectrophotometer with samples mounted between KBr disks. The $^1H$ NMR (400 MHz) and $^{13}C$ NMR (100 MHz) spectra were recorded on a Bruker Avance NMR spectrometer in $CDCl_3$ and DMSO-$d_6$ solutions. Mass spectra were recorded on an Agilent Technology (HP) 5973 instrument (ionizing voltage 70 eV). Elemental analyses were done on a Carlo-Erba EA1110 CHNO-S analyzer. The progress of the reaction was monitored using TLC with silica–gel SIL G/UV 254 plates. Products were characterized by comparing their physical and spectral data to those of authentic samples.

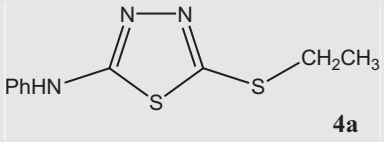
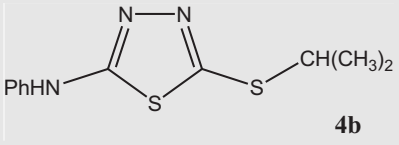
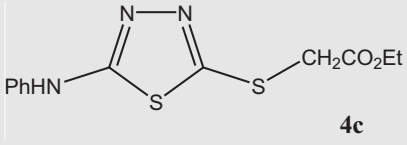
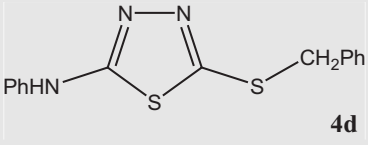
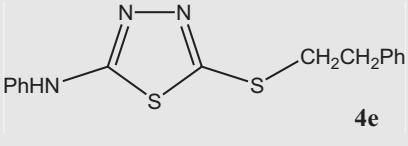
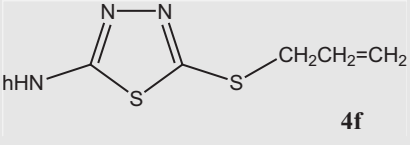
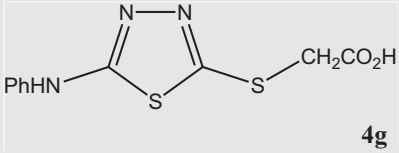
### 3.2. Typical procedure for the synthesis of 5-phenylamino-1,3,4-thiadiazole-2-thione 2

A mixture of phenylthiosemicarbazide (1.0 mmol) and carbon disulfide (3.0 mmol) in DMF (2.0 mL) was stirred for 15 min at room temperature. The resulting reaction mixture was then heated at 70 °C until ring closure was complete (7 h). Progress of reaction was checked by TLC (ethyl acetate: *n*-hexane (1:2)). After cooling to room temperature, the reaction mixture was added dropwise to ice cold water (15 mL) to yield a solid (title compounds) which was collected by filtration and washed with water. Mp 207–209 °C. IR (KBr) $cm^{-1}$: 3123, 2360, 1599, 1569, 1473, 1295. $^1H$ NMR (400 MHz, DMSO-$d_6$): *δ:* 13.70 (1H, s), 10.16 (1H, s), 7.43–7.32 (4H, m), 7.02 (1H, m). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): *δ:* 181.6, 159.8, 140.2, 129.6,

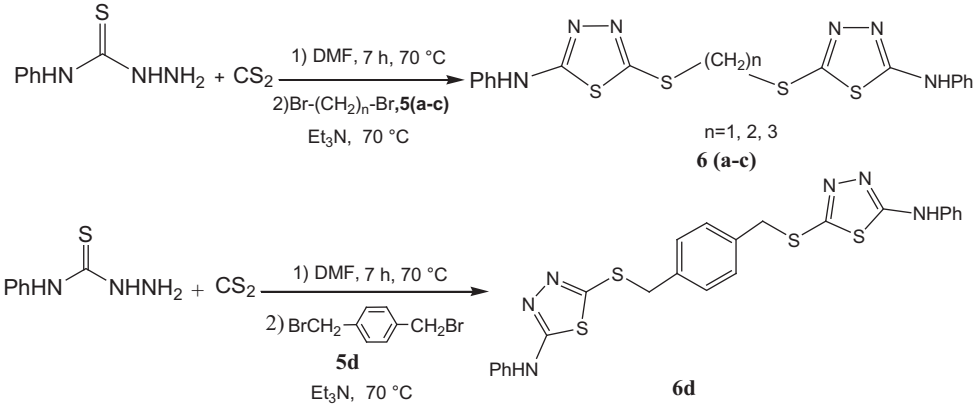



**Scheme 2** 2-phenylamino-5-alkylthio-1,3,4-thiadiazole derivatives synthesis.

**Table 2** One-pot synthesis of 2-phenylamino-5-alkylthio-1,3,4-thiadiazole **4(a–g)** from phenylthiosemicarbazide **1** and alkyl halides **3(a–g)** in the presence of $Et_3N$.

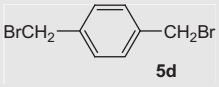
| Entry | R-X, 3 | Product, 4 | Time (h) | Yield[a](%) |
|---|---|---|---|---|
| 1 | $CH_3CH_2$-I, **3a** |  **4a** | 4.45 | 85 |
| 2 | $(CH_3)_2CH$-Br, **3b** |  **4b** | 7 | 78 |
| 3 | $EtO_2CCH_2$-Br, **3c** |  **4c** | 6 | 80 |
| 4 | $PhCH_2$-Cl, **3d** |  **4d** | 4.30 | 83 |
| 5 | $PhCH_2CH_2$-Br, **3e** |  **4e** | 7 | 74 |
| 6 | $CH_2{=}CHCH_2$-Br, **3f** |  **4f** | 7 | 87 |
| 7 | $HO_2CCH_2$-Cl, **3g** |  **4g** | 3 | 70 |

[a] Isolated yield.




**Scheme 3** bis-(2-phenylamino-5-alkylthio)-1,3,4-thiadiazole derivatives synthesis.

**Table 3** One-pot synthesis of bis-(2-phenylamino-5-alkylthio)-1,3,4-thiadiazole **6(a–d)** from phenylthiosemicarbazide **1** and alkyl dihalides **5(a–d)** in the presence of $Et_3N$.

| Entry | Alkyl dihalide, **5(a–c)** | Product, **6(a–c)** | Time (h) | Yield[a](%) |
|---|---|---|---|---|
| 1 | Br-$CH_2CH_2$-Br, **5a** | **6a** ($n$ = 1) | 4.0 | 68 |
| 2 | Br-$CH_2(CH_2)_2CH_2$-Br, **5b** | **6b** ($n$ = 2) | 7.0 | 62 |
| 3 | Br-$CH_2(CH_2)_4CH_2$-Br, **5c** | **6c** ($n$ = 3) | 6.0 | 67 |
| 4 |  **5d** | **6d** | 8.0 | 74 |



[a] Isolated yield.

122.7, 117.8. MS (EI, 70 eV) $m/z$ (%) 209 (100), 150 (24), 136 (24), 128 (16), 118 (19), 104 (26), 91 (15), 77 (92), 64 (42), 59 (20), 51(44). Anal. calcd for: $C_8H_7N_3S_2$; C, 45.91; H, 3.37; N,20.08%. Found: C, 45.73; H, 3.45; N, 20.26%.

### *3.3. General procedure for the synthesis of 2-phenylamino-5-alkylthio-1,3,4-thiadiazole derivatives **4(a–g)** and **6(a–d)***

A mixture of phenylthiosemicarbazide (1.0 mmol) and carbon disulfide (3.0 mmol) in DMF (2.0 mL) was stirred for 15 min at room temperature. The resulting reaction mixture was then heated at 70 °C until ring closure was complete (7 h). Alkyl halide (1.2 mmol) and $Et_3N$ (4 mmol) were then added to the reaction mixture and stirred again at 70 °C until the reaction was completed as monitored by TLC (ethyl acetate:*n*-hexane, 1:2). After cooling to room temperature, the reaction mixture was added dropwise to ice cold water (15 mL) to yield a solid (title compounds) which was collected by filtration and washed with water. In order to synthesize bis-(2-phenylamino-5-alkylthio)1,3,4-thiadiazole derivatives, 0.5 mmol of alkyl dihalides (BrYBr) was used according to the general procedure.

#### *3.3.1. Table 2, Entry 1, **4a***

A solid, Mp 138–140 °C. IR (KBr) $cm^{-1}$: 3248, 1604, 1562, 1252, 1087. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$: 10.36 (1H, br s), 7.45–7.38(4H, m), 7.14–7.10 (1H, m), 3.21(2H, q, $J$ = 7.6 Hz), 1.47 (3H, t, $J$ = 7.6 Hz). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$: 167.5, 152.4, 140.3, 129.6, 123.5, 118.1, 29.6, 14.9. MS (EI, 70 eV) $m/z$ (%) 237(100), 234(90), 209(27), 204(50), 150(27), 136(67), 118(29), 109(18), 77(94), 51(35), 41(23). Anal. calcd for: $C_{10}H_{11}N_3S_2$; C, 50.60; H, 4.67; N,17.70%. Found: C, 50.43; H, 4.45; N, 17.86%.

#### *3.3.2. Table 2, Entry 2, **4b***

A solid, Mp 115–116 °C. IR (KBr) $cm^{-1}$: 3139, 1615, 1599, 1500, 1099. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$: 10.52 (1H, br s), 7.62 (2H, t, $J$ = 7.6 Hz), 7.35 (2H, t, $J$ = 7.6 Hz), 7.01(1H, t, $J$ = 7.6 Hz), 3.65 (1H, sept, $J$ = 6.8 Hz), 1.35 (6H, d, $J$ = 6.8 Hz). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$: 165.9, 151.7, 140.9, 129.6, 122.5, 117.9, 40.4, 23.49. MS (EI, 70 eV) $m/z$ (%) 251(84), 218(20), 210(17), 209(100), 150(30), 136(28), 104(12), 91(8), 77(38), 43(27). Anal. calcd for: $C_{11}H_{13}N_3S_2$; C, 52.56; H, 5.21; N, 16.72%. Found: C, 52.39; H, 5.08; N, 16.51%.

#### *3.3.3. Table 2, Entry 3, **4c***

A solid, Mp 100–102 °C. IR (KBr) $cm^{-1}$: 3248, 1603, 1503, 1444, 1088. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$: 10.94 (1H, br s), 7.47–7.37(4H, m), 7.12(1H, m), 4.23(2H, q, $J$ = 7.2 Hz), 3.96 (2H, s), 1.28 (3H, t, $J$ = 7.2 Hz). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$: 168.4, 168.2, 150.2, 140.3, 129.7, 123.6, 118.0, 62.1, 36.5, 14.2. MS (EI, 70 eV) $m/z$ (%) 295(85), 250(12), 222(48), 221(47), 150(52), 136(88), 118(84), 91(42), 77(100),

51(71), 42(45%). Anal. calcd for: $C_{12}H_{13}N_3O_2S_2$; C, 48.79; H, 4.44; N, 14.23%. Found: C, 48.53; H, 4.51; N, 14.09%.

### 3.3.4. Table 2, Entry4, **4d**

A solid, Mp 144–145 °C. IR (KBr) $cm^{-1}$: 3242, 1601, 1573, 1087. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$: 10.39 (1H, s), 7.59–7.01 (10H, m), 4.42 (2H, s). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$: 165.4, 152.6, 140.8, 137.4, 129.6, 129.5, 129.0, 128.0, 122.5, 117.8, 38.5. MS (EI, 70 eV) $m/z$ (%) 299(85), 266(36), 148(48), 136(18), 91(100), 77(32), 65(20), 51(19%). Anal. calcd for: $C_{15}H_{13}N_3S_2$; C, 60.17; H, 4.38; N, 14.03%. Found: C, 60.29; H, 4.19; N, 14.27%.

### 3.3.5. Table 2, Entry 5, **4e**

A solid, Mp 125–127 °C. IR (KBr) $cm^{-1}$: 3305, 1598, 1503, 1068. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$: 10.42 (1H, s), 7.62–7.00 (10H, m), 3.42(2H, t, $J$ = 7.6), 3.01 (2H, t, $J$ = 7.6). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$: 165.1, 153.2, 140.9, 140.0, 129.6, 129.1, 128.9, 126.9, 122.4, 117.9, 35.6, 35.5. MS (EI, 70 eV) $m/z$ (%) 313(15), 209(100), 150(26), 136(30), 118(28), 105(55), 91(53), 77(95), 69(29), 51(40), 41(30). Anal. calcd for: $C_{16}H_{15}N_3S_2$; C, 61.31; H, 4.82; N, 13.41%. Found: C 61.19; H, 4.89; N, 13.38%.

### 3.3.6. Table 2, Entry 6, **4f**

A solid, Mp 98–99 °C. IR (KBr) $cm^{-1}$: 3255, 1621, 1601, 1572, 1087. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$: 11.00 (1H, br s), 7.60–7.11 (5H, m), 6.01 (1H, m), 5.28(2H, dd, $J$ = 16.8 Hz, $J$ = 1.2 Hz), 5.20 (2H, d, $J$ = 10 Hz), 3.79(2H, d, $J$ = 7.2). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$: 168.1, 151.2, 140.4, 132.6, 129.7, 123.5, 119.3, 118.0, 38.2. MS (EI, 70 eV) $m/z$ (%) 249(76), 235(28), 234(100), 136(54), 118(19), 109(13), 98(15), 77(70), 64(19), 51(22), 41(33). Anal. calcd for: $C_{11}H_{11}N_3S_2$ ; C, 52.98; H, 4.45; N, 16.85%. Found: C, 53.14; H, 4.57; N, 17.01%.

### 3.3.7. Table 2, Entry 7, **4g**

A solid, Mp 190–192 °C. IR (KBr) $cm^{-1}$: 3259, 1626, 1600, 1576, 1467, 1088. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$: 13.0 (1H, br s), 10.39 (1H, br s), 7.58 (2H, d, $J$ = 7.6 Hz), 7.35 (2H, t, $J$ = 7.2 Hz), 7.01(1H, t, $J$ = 7.2 Hz), 4.11 (4H, s). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$: 170.0, 165.3, 152.6, 140.9, 129.6, 122.5, 117.8, 36.2. MS (EI, 70 eV) $m/z$ (%) 267(79), 223(41), 221(28), 190(68), 150(33), 136(68), 118(43), 91(20), 77(100), 51(38), 45(27). Anal. calcd for: $C_{10}H_9N_3O_2S_2$; C, 44.93; H, 3.39; N, 15.72%. Found: C, 44.79; H, 3.21; N, 15.58%.

### 3.3.8. Table 3, Entry 1, **6a**

A solid, Mp 236–238 °C. IR (KBr) $cm^{-1}$: 3251, 1613, 1540, 1085. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$: 10.43 (2H, s), 7.58(4H, d, $J$ = 7.6), 7.34(4H, t, $J$ = 7.6), 7.01(1H, t, $J$ = 7.6), 3.51(4H, s). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$: 165.4, 152.2, 140.8, 129.6, 122.5, 117.9, 34.1. MS (EI, 70 eV) $m/z$ (%) 444(3), 392(31), 214(100), 209(66), 139(48), 111(31), 91(55), 88(69), 77(91), 51(42), 42(31). Anal. calcd for: $C_{18}H_{16}N_6S_4$; C, 48.62; H, 3.63; N, 18.90%. Found: C, 48.81; H, 3.51; N, 18.76%.

### 3.3.9. Table 3, Entry 2, **6b**

A solid, Mp 197–200 °C. IR (KBr) $cm^{-1}$: 3264, 1600, 1546, 1511, 1242, 1087. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$: 10.47(2H, br s), 7.59 (4H, d, $J$ = 8.0 Hz), 7.34 (4H, t, $J$ = 7.6 Hz), 7.01 (2H, t, $J$ = 7.2 Hz), 3.45 (4H, s), 1.84 (4H, s). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$: 165.2, 153.2, 140.9, 129.6, 122.4, 117.8, 33.9, 28.4. MS (EI, 70 eV) $m/z$ (%) 472(4), 264(42), 209(94), 150(25), 136(41), 118(51), 104(20), 91(25), 77(100), 65(22), 51(39). Anal. calcd for: $C_{20}H_{20}N_6S_4$: C, 50.82; H, 4.26; N, 17.78%. Found: C, 50.69; H, 4.37; N, 17.94%.

### 3.3.10. Table 3, Entry 3, **6c**

A solid, Mp 174–176 °C. IR (KBr) $cm^{-1}$: 3261, 1602, 1512, 1501, 1244, 1087. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$: 10.39 (2H, s), 7.59–7.34 (8H, m), 7.00 (2H, m), 3.16 (4H, s), 1.69 (4H, s), 1.42 (4H, s). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$: 165.0, 153.4, 140.9, 129.6, 122.4, 117.8, 34.4, 29.4, 27.8. MS (EI, 70 eV) $m/z$ (%) 500 (3), 264(57), 236(22), 209(35), 178(74), 149(44), 118(44), 97(41), 83(48), 69(100). 43(88). Anal. calcd for: $C_{22}H_{24}N_6S_4$, C, 52.77; H, 4.83; N, 16.78%. Found: C, 52.53; H, 5.03; N, 16.98%.

### 3.3.11. Table 3, Entry 4, **6d**

A solid, Mp 233–236 °C, IR (KBr) $cm^{-1}$: 3248, 1600, 1572, 1088. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$: 10.40 (2H, s), 7.58 (4H, d, $J$ = 7.6), 7.39 (4H, s), 7.34 (4H, t, $J$ = 7.6 Hz), 7.00 (2H, t, $J$ = 7.2), 4.42 (4H, s). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$: 165.4, 152.6, 140.8, 136.7, 129.7, 129.6, 122.5, 117.9, 38.11. MS (EI, 70 eV) $m/z$ (%) 520(2), 312(15), 209(93), 176(19), 150(22), 136(43), 118(31), 104(47), 91(38), 77(100), 51(40%). Anal. calcd for: $C_{24}H_{20}N_6S_4$, C, 55.36; H, 3.87; N, 16.14%. Found. C, 55.48; H, 3.61; N, 15.99%.

## 4. Conclusion

In conclusion, a novel and fairly efficient chemoselective one-pot method has been developed for the synthesis of 2-phenylamino-5-alkylthio-1,3,4-thiadiazole and bis-(2-phenylamino-5-alkylthio-)1,3,4-thiadiazole derivatives from phenylthiosemicarbazide and $CS_2$. The main advantages of this method are its safe, easy handling and work-up, simplicity, chemoselectivity, economic feasibility and good to high yields. Also, for the synthesis of an extended range of 1,3,4-thiadiazole derivatives, a variety of alkyl halides, such as alkyl and α-halo acid and ester, benzyl, allyl, and alkyl dihalides are used.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2014.10.029.

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